

# Status Update on PR 1410 – Hydrogen Fluoride Storage and Use at Petroleum Refineries



Governing Board  
Meeting

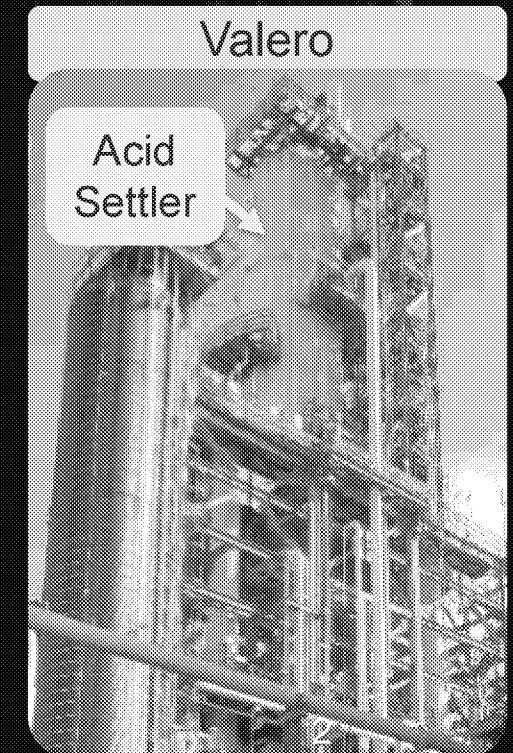
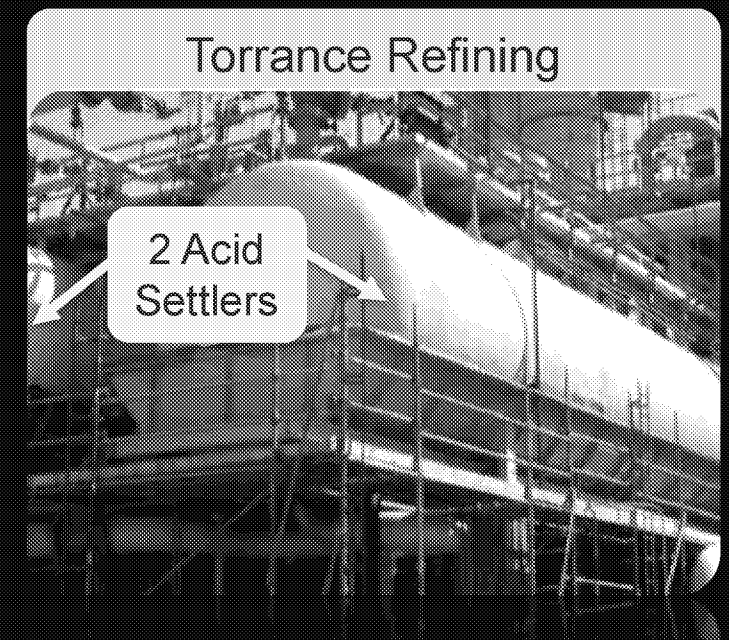
February 1, 2019  
Diamond Bar, California

# HF Background

- Hydrogen fluoride (HF) is a strong, potentially lethal acid
- HF is used to produce alkylate which is a blending component of high-octane gasoline
- Used at two California refineries: Torrance Refining and Valero
- Both refineries use modified HF (MHF), designed to reduce its exposure

## Approximate Volumes (gallons)

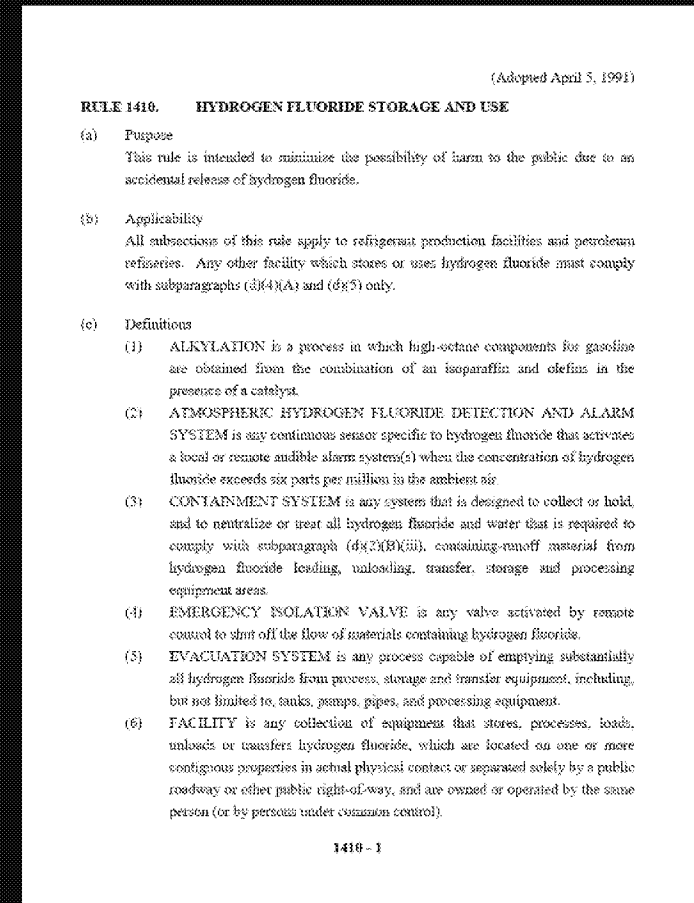
	Valero (Wilmington)	Torrance Refining
Storage on-site	55,000	25,000
Use in acid settlers	7,000 with baffle	12,000 in two tanks



# Regulatory Background

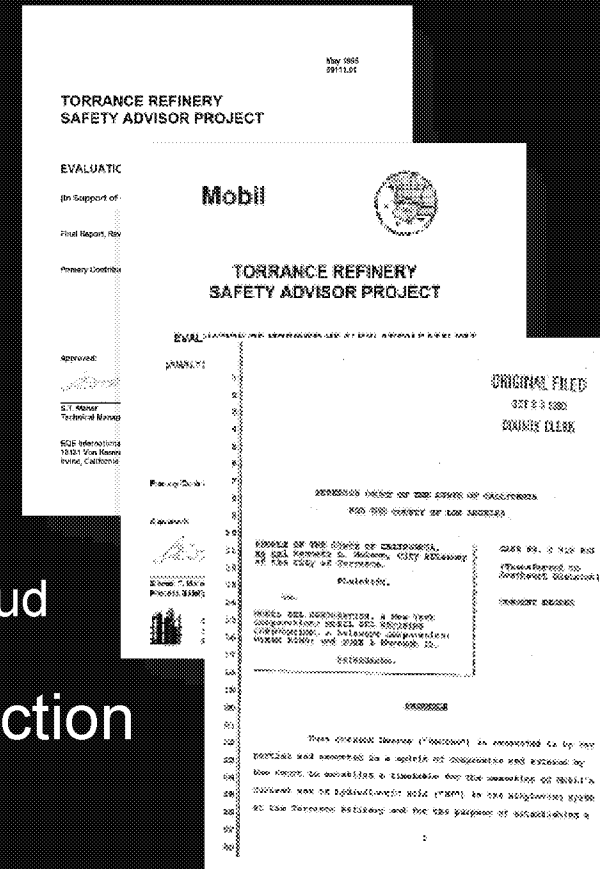
- April 1991 Board adopted Rule 1410 – Hydrogen Fluoride Storage and Use
  - ❑ Established a 7-year phase-out of HF unless a performance standard could be achieved
  - ❑ Required interim control measures
- Lawsuit challenged Rule 1410
  - ❑ SCAQMD's authority to phase out HF was upheld<sup>1</sup>
    - “[T]he Legislature clearly intended to vest AQMD with the authority to adopt preemptive measures designed to prevent air pollution episodes . . . .”
  - ❑ Rule invalidated due to procedural error in circulating CEQA document

<sup>1</sup> *Ultramar, Inc. v. South Coast Air Quality Management District*, 17 Cal. App. 4th 706-12 (1993).



# Decision Not to Pursue Re-Adoption of Rule 1410

- 1991 ● Mobil Refinery<sup>2</sup> entered into a court consent decree
- Phase-out of HF by 1997 or
  - Allow use of MHF if demonstrates no formation of dense vapor cloud
- 1999 ● Consent decree was changed to allow a significant reduction of the modifier
- 2003 ● SCAQMD signed MOU with Ultramar<sup>3</sup> to phase-out HF and allow use of MHF
- 2017 ● Torrance Refining provided SCAQMD with confidential information about MHF



<sup>2</sup> Currently Torrance Refining Company

<sup>3</sup> Ultramar is currently Valero

# Events Leading to the Investigative Hearing in April 2017

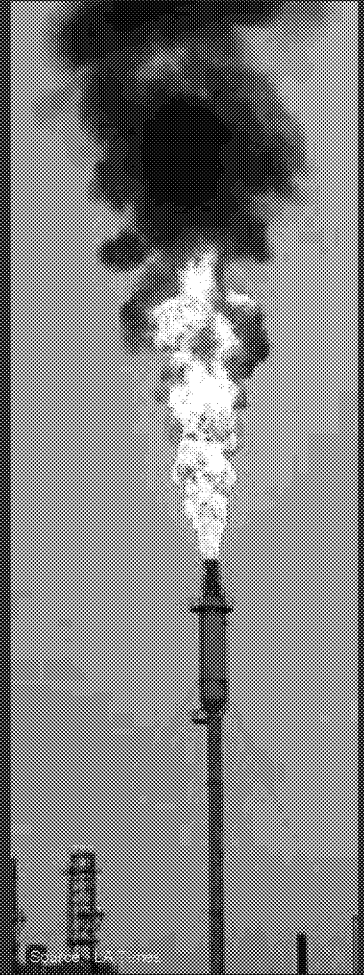
**2015**

“Near Miss”  
40 ton  
debris lands  
within 5 feet  
from MHF  
tanks at  
Torrance  
Refining



**2016-2017**

Series of large  
flaring events  
and fire event  
that raised  
concerns about  
safety  
at Torrance  
Refining



# 10 MHF Leaks Since 2017



<sup>4</sup> HF point sensors can only measure up to 10 ppm. Concentrations could have been higher.

<sup>5</sup> 5 gallons of HF released at loading rack. No HF point sensors at loading rack. Closest HF point sensor is ~ 25 feet.

# Public Process Following Investigative Hearing

## 1,300+ Comment Letters and Emails

- 500+ commenters opposing a phase-out
- 800+ commenters supporting a phase-out
- 7 letters from elected officials

## 4 Refinery Committee Meetings

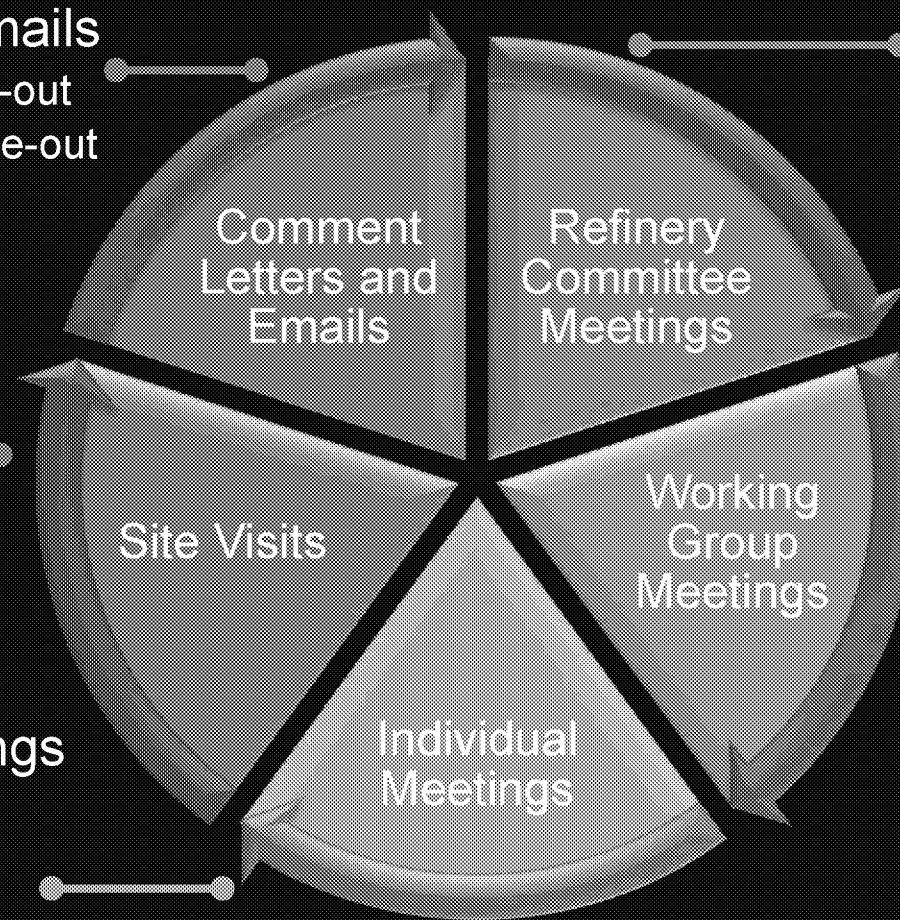
- ~ 600 attendees per meeting
- ~ 80 commenters per meeting
- 8 expert presentations

## Multiple Site Visits

- Observed current mitigation and safety measures at both refineries

## 19 Individual Stakeholder Meetings

- 12 meetings with refineries
- 5 meetings with community groups
- 2 meetings with EPA/Cal OSHA





# Why is HF usage at refineries a concern?

**Refineries use large volumes of MHF...**

**2 inch hole could release  
1,000 gallons in 2 minutes<sup>6</sup>**

<sup>6</sup> Based on Goldfish Study, Test 1 – Unmitigated release of HF

# Ground hugging cloud upon release...



## Maximum concentration below 8 feet<sup>7</sup> within breathing height

<sup>7</sup> Based on Goldfish Study, Test 1 – Unmitigated release of HF

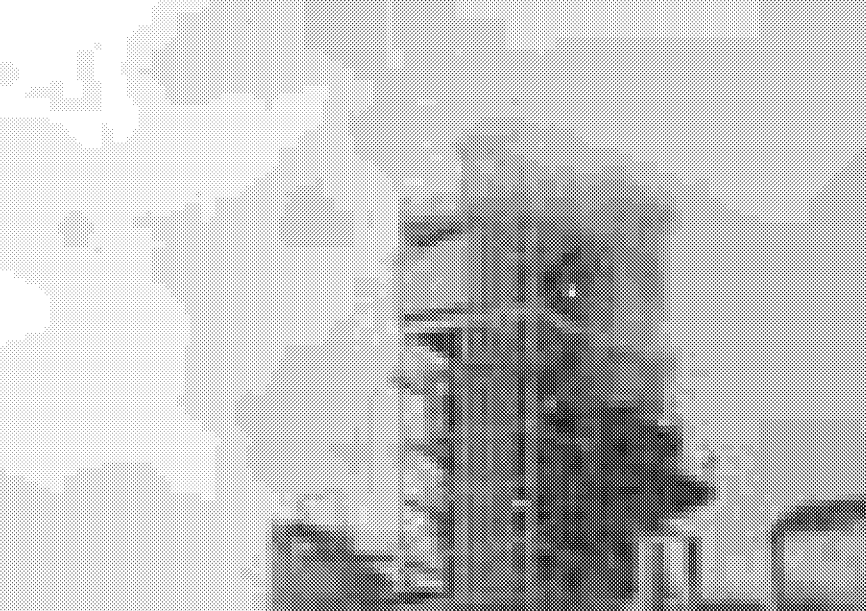


**Rapid expansion of a  
vapor cloud upon  
release...**

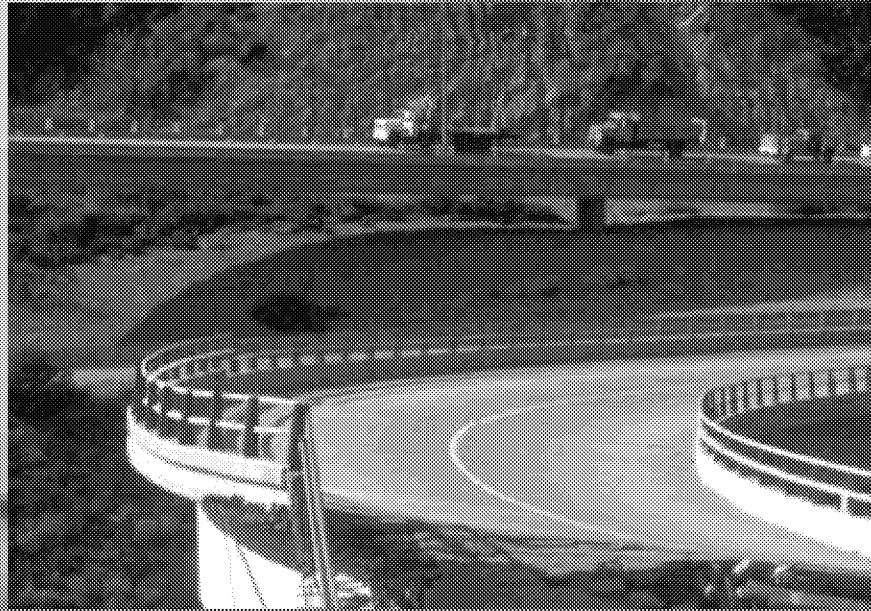
**Tests have shown  
lethal concentrations  
can travel 2 miles<sup>8</sup>**

<sup>8</sup> Based on Goldfish Study, Test 1, unmitigated, 1.65 inch release. Lethal concentration of 170 ppm for 10 minutes, USEPA Acute Exposure Guideline Level. 11

**Large-scale unexpected  
incidents such as...**



**System Failures**

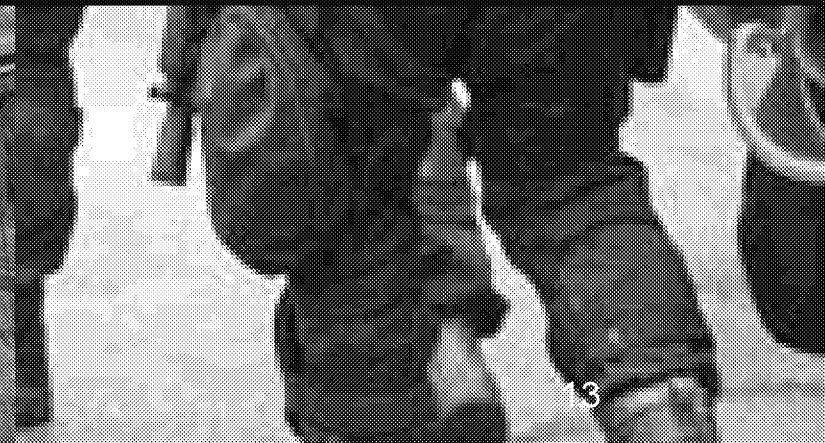


**Natural Disasters**



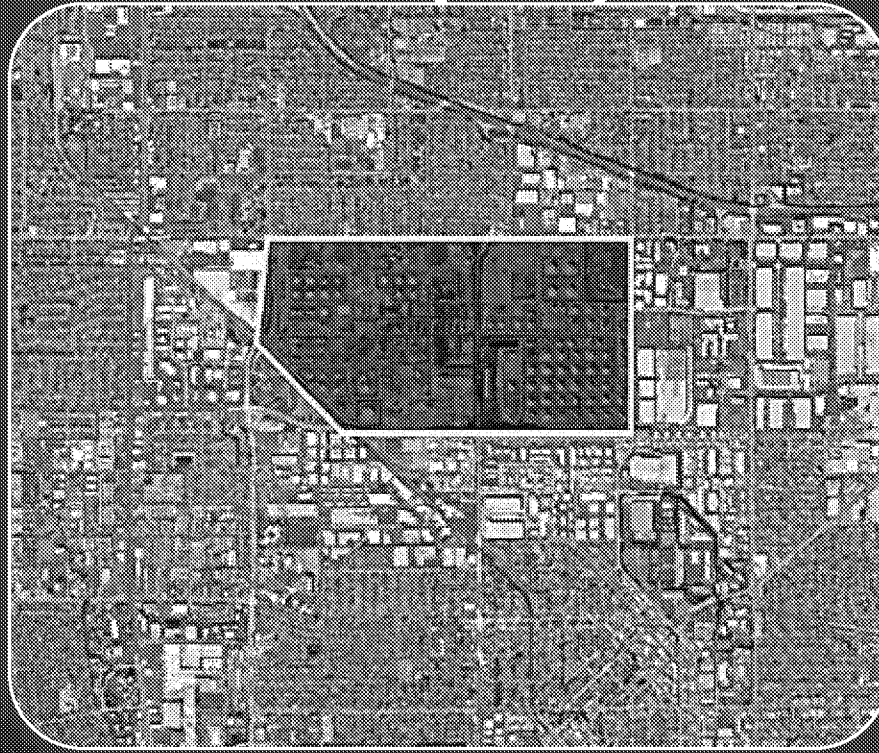
**Intentional Acts**

***Can lead to cascading failures***



**High  
population  
densities...  
Greater  
potential for  
widespread  
human harm**

## **Torrance Refining Company**



**245,000 People within 3 Miles  
Nearest Residence ~0.3 miles**

## **Valero Wilmington Refinery**



**153,000 People within 3 Miles  
Nearest Residence ~0.8 miles**

# Uniquely hazardous health effects that result in deep tissue and bone damage...



**Requires immediate and  
specialized treatment**

In 1986 Amoco and Allied  
Signal Corporation  
sponsored the "Goldfish"  
tests to assess HF release

Single release point was  
1.65 inches (size of a golf  
ball)

1,000 gallons was  
released in 2 minutes

Ground hugging cloud  
travelled at wind speed of  
18 feet per second

Cloud rapidly expanded  
upon release

HF concentration was  
twice the lethal level at 2  
miles from release point

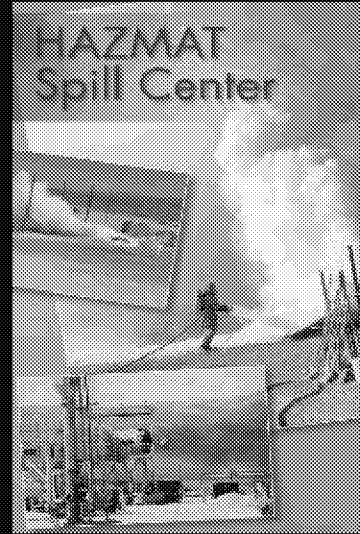
100% remained airborne



Courtesy: Dr. Ronald Koopman

# Field Tests

- Nevada Test Site
  - ❑ Goldfish test - large scale outdoor testing
  - ❑ Hawk Test - smaller wind tunnel tests on water spray mitigation
- Quest Consultants Inc. conducted two field tests for MHF<sup>9</sup> (1992-1993) in Oklahoma
  - ❑ Mobil and Phillips
  - ❑ Texaco and UOP



Nevada Test Site		
Name	Year	Material
Avocet	1978	LNG
Burro	1980	LNG
Coyote	1981	LNG
Desert Tortoise	1983	Ammonia
Eagle	1983	N <sub>2</sub> O <sub>4</sub>
Goldfish	1986	HF
Hawk	1988	HF

<sup>9</sup> Both field tests were not at the current operating conditions (temperature, pressure, and additive concentration) used at refineries.

# Acute Exposure Levels for HF for 10 Minutes<sup>10</sup>

## Mild Health Effects

- 1 ppm
- Not disabling
- Notable discomfort
- Reversible health effects

## Serious Health Effects

- 95 ppm
- Impaired ability to escape
- Long-lasting health effects
- Irreversible health effects

## Lethal Health Effects

- 170 ppm
- Life threatening
- Death

# HF Levels Measured in Goldfish Study



<sup>11</sup> USEPA Acute Exposure Guideline Levels for 10 minutes exposure to HF

A faded, grayscale background image showing a person's head and shoulders in profile, shouting or singing with their mouth wide open. A large, semi-transparent 'NO' sign is overlaid on the image, partially obscuring the person's face and the background.

# **How much safer is MHF than HF?**

# Background on MHF

- Jointly developed by Mobil/Phillips in early 90's
- Modifier added to HF to reduce vapor-forming tendency
- Intent was for most of HF to rainout or fall to the ground
  - ❑ Initial additive concentration was ~30 percent, but led to "operational instability"<sup>12</sup>
  - ❑ Additive concentration decreased to ~7 percent
- Torrance Refining claims that 50% of MHF will rainout

# SCAQMD's Analysis of MHF

- Based on a review of technical documents and discussions with Torrance Refinery
  - Some, but uncertain, benefits of MHF
  - At most 35 percent benefit, but likely less
- No testing conducted at current operating conditions (additive concentration, pressure, and temperature)
- Most of the data is not publicly available
- Use of MHF is only one of many mitigation measures, but alone does not provide adequate safety for workers and community

# HF and MHF Have Similar Concerns

- Ability of MHF to prevent formation of a vapor/aerosol cloud is highly uncertain
- Release of MHF will result in exposure to HF with same health effects
  - ❑ Any rainout will be HF liquid droplets
  - ❑ HF vapor cloud will still form
  - ❑ HF and MHF have same hazards and medical treatment

**Material Safety Data Sheet****HYDROFLUORIC ACID, ANHYDROUS****1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION****PRODUCT NAME:** Hydrofluoric Acid, Anhydrous**OTHER/GENERIC NAMES:** HF, Anhydrous HF, AHF, Hydrogen Fluoride, HF Acid**PRODUCT USE:** Chemical Derivatives, Alkylation Catalyst**MANUFACTURER:** Honeywell International  
Industrial Fluorides  
101 Columbia Road  
Box 1053  
Morristown, New Jersey 07962-1053**Material Safety Data Sheet****MODIFIED HYDROFLUORIC ACID****1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION****PRODUCT NAME:** Modified Hydrofluoric Acid**OTHER/GENERIC NAMES:** MHF, Modified HF, Modified Hydrogen Fluoride, Modified HF Acid, Additized HF**PRODUCT USE:** Alkylation Catalyst**MANUFACTURER:** Honeywell International  
Industrial Products  
101 Columbia Road  
Box 1053

**EMERGENCY OVERVIEW:** Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.

10000000

**3. HAZARDS IDENTIFICATION**


**EMERGENCY OVERVIEW:** Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.

Hydrofluoric Acid  
Sulfonate7664-39-3 85  
126-33-0 15

Trace impurities and additional material names not listed above may also appear in the Regulatory Information Section 15 towards the end of the MSDS. These materials may be listed for local "Right-To-Know" compliance and for other reasons.

**3. HAZARDS IDENTIFICATION**

**EMERGENCY OVERVIEW:** Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.



# The Discussion

# Direction from Refinery Committee

- Enhanced mitigation measures; and
  - Phase-out MHF and explore option for a performance standard
- 
- ```
graph LR; A["• Enhanced mitigation measures; and  
• Phase-out MHF and explore option for a performance standard"] --> B["Develop a Rule"]; A --> C["Develop an MOU"];
```

Develop a Rule

**OR**

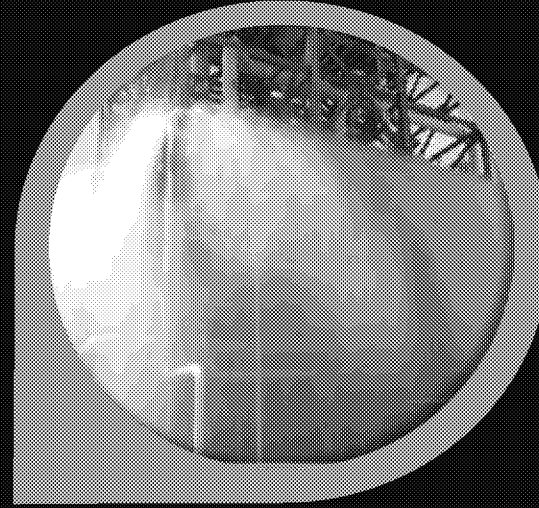
Develop an MOU

# Areas of General Agreement

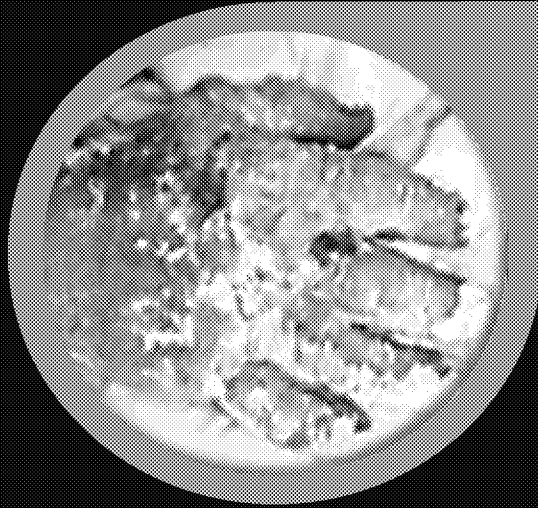
HF and MHF  
are dangerous  
acids



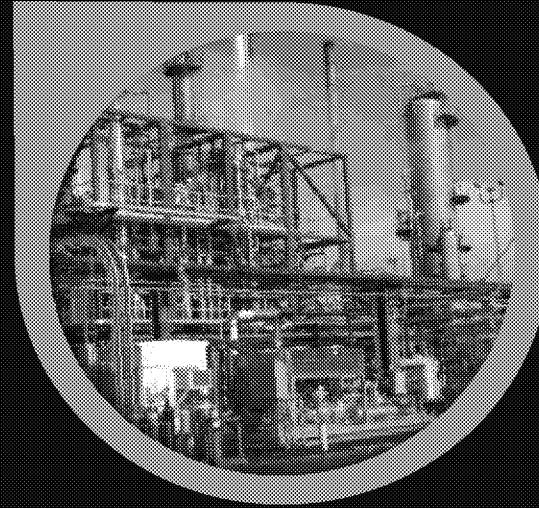
Enhanced  
mitigation  
measures are  
needed



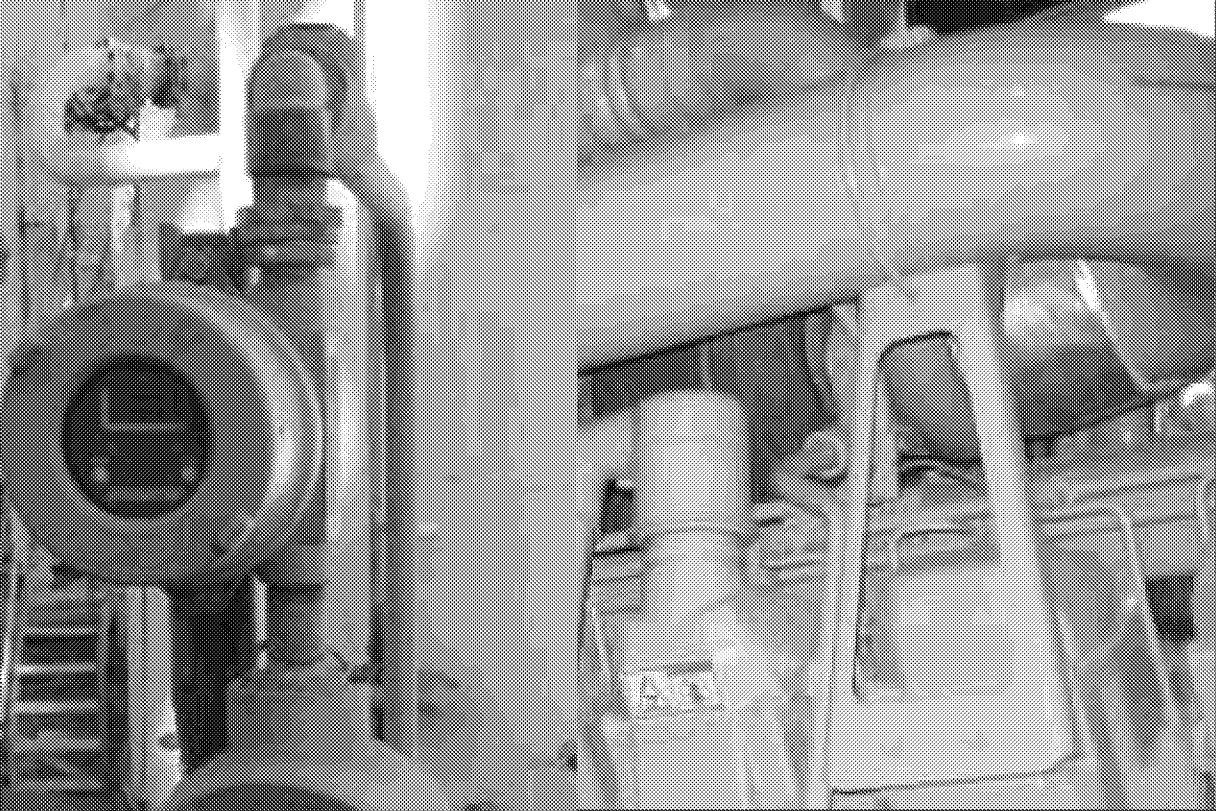
HF and MHF  
have the same  
health effects



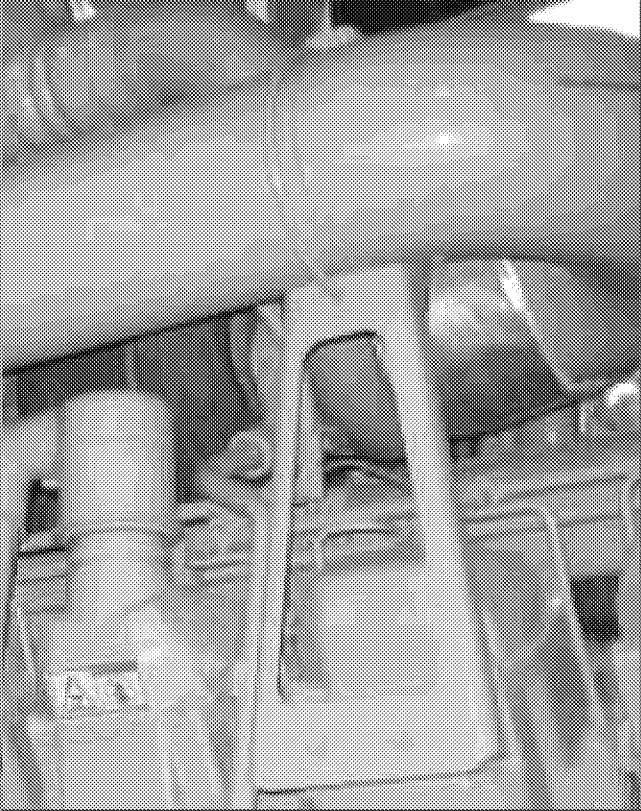
Other than sulfuric  
acid, additional  
time needed for  
other alternative  
technologies



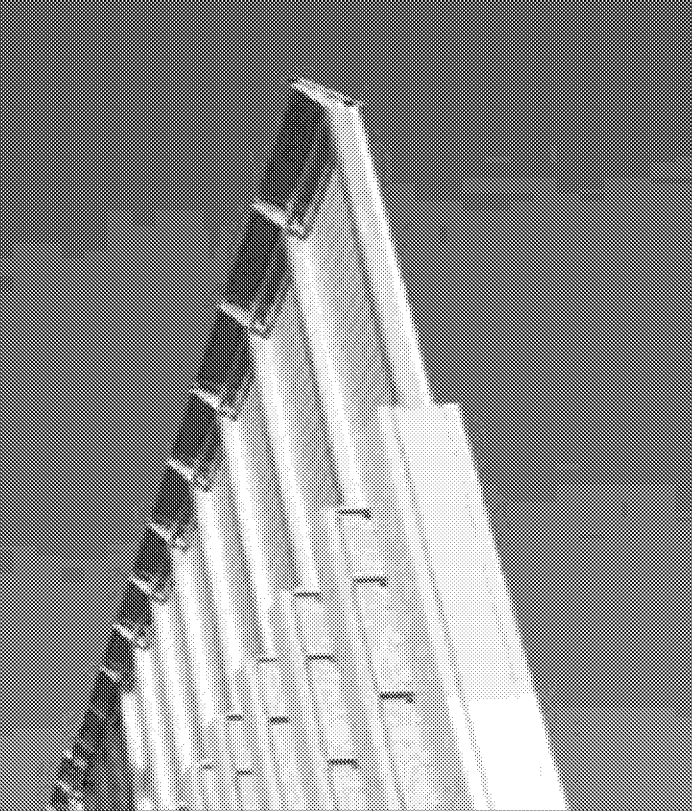
# Overview of Enhanced Mitigation



Response  
Time



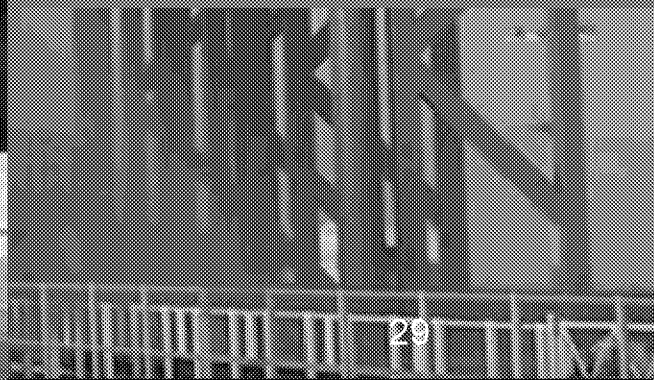
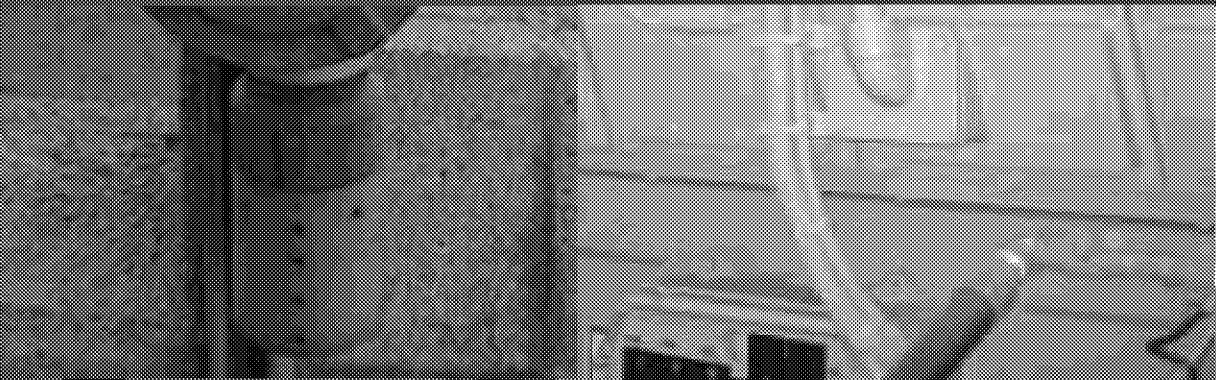
Added  
Redundancy



Enhanced  
Barriers



Enhanced  
Water



# Alternative HF Technologies



## Sulfuric Acid (Conventional)

- At 39 US refineries
- Safer than HF, but 50 more truck trips per day



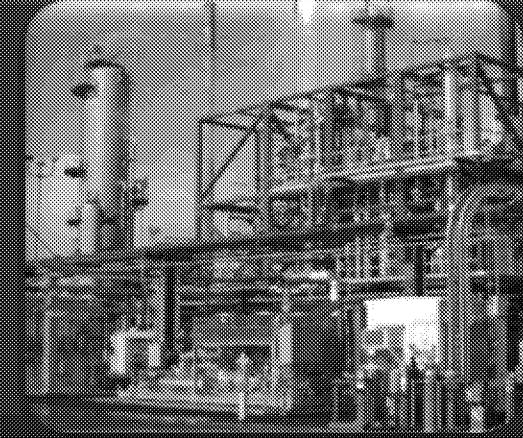
## Sulfuric Acid (Advanced)

- CDAlky uses 30-50% less acid – commercially proven
- ConvEx designed for HF conversion – not commercially proven



## Solid Acid Catalyst

- Petrochemical plant in China
- 2,700 bpd startup in 2015



## Ionic Liquid Catalyst

- Chevron, Salt Lake City
- Small pilot plant in 2005
- 5,000 bpd HF Alkylation conversion startup in 2020

# Costs and Potential Market Impacts

- Torrance Refining's cost estimate of grassroots sulfuric acid unit<sup>13</sup>
  - \$600 million for alkylation unit
  - \$300 million for acid regeneration
- Valero has commented their facility has space constraints
- Advanced sulfuric acid units are expected to be substantially less
- Alternative technologies
  - Cost unknown
  - Torrance Refining views commercially viable as constructed at scale to California standards for two four-year turnaround cycles (Minimum of 12 years)
- Potential impacts to gasoline supply and cost
  - Any impacts would be temporary
  - Planned phase-out is different than an unplanned shutdown – less disruptive

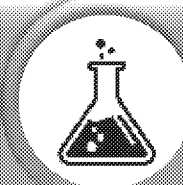
<sup>13</sup> Burns and McDonnell - Alkylation Study & Estimate, 2017

# Discussion on MHF Phase-Out

No Phase-out

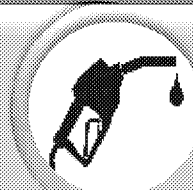
Yes Phase-out

Alternative technologies not commercially proven



Longer implementation schedule with a technology assessment

Phase-out could result in a gasoline shortage



Lead time to plan - other options for alkylate supply

Refineries state they have and will continue to use MHF safely



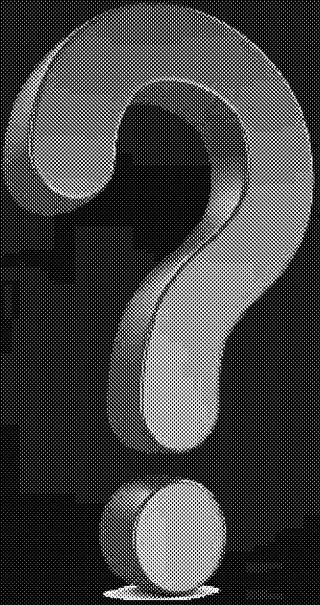
Uncertain a consequential release can be mitigated

Refinery estimate: \$900 million (Alkylation Unit and Acid Plant)



Lives at risk – cost of large release must be considered

# Uncertain that Enhanced Mitigation Can Protect the Community

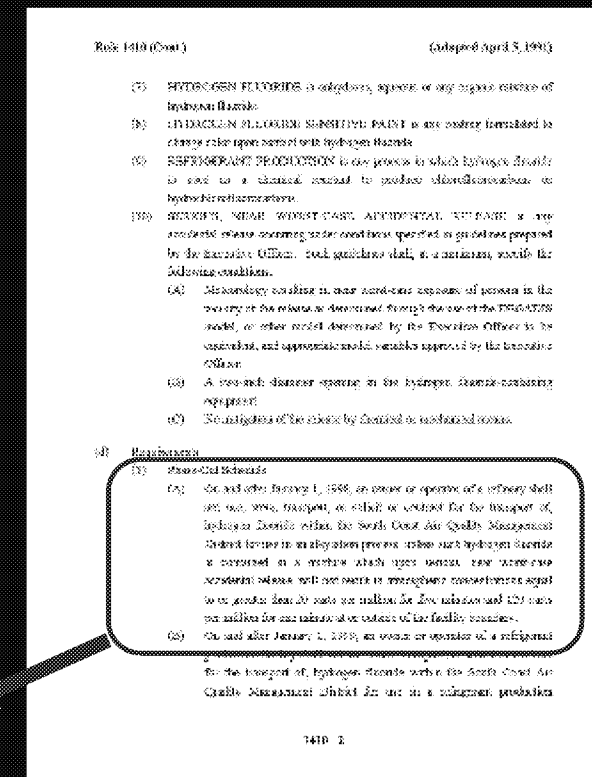
- 
- Can consequential release be mitigated?
  - Can mitigation capture initial cloud?
  - Can water be deployed rapidly?
  - Can the mitigation system target exact location?
  - Can the refineries supply enough water?
  - Can sufficient redundancy guard against system failure?

The background of the slide is a grayscale image of an industrial facility, likely a power plant or refinery, featuring several tall smokestacks emitting plumes of smoke or steam. A faint, light-gray grid pattern is overlaid on the entire image. The main title is centered in a large, bold, black sans-serif font.

# **What is a Performance Standard?**

# Performance Standard

- Benchmark that refineries would need to meet for continued use of MHF
- Needed to ensure enhanced mitigation can protect community
- Possible examples:
  - ❑ Concentration limit at fenceline or nearest receptor
  - ❑ Demonstrate MHF will not form dense vapor cloud
- 1991 Rule 1410 included a performance standard:
  - ❑ 20 ppm for 5 minutes; and
  - ❑ 120 ppm for 1 minute at the fenceline

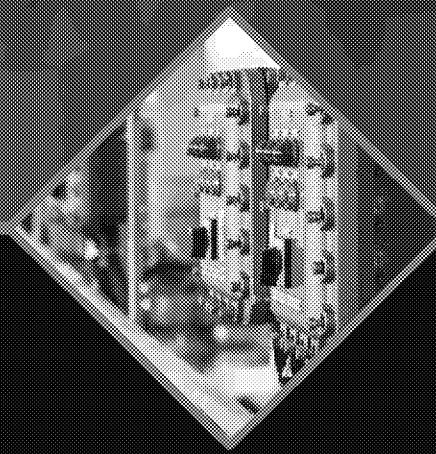


# Three Key Elements of Performance Standard



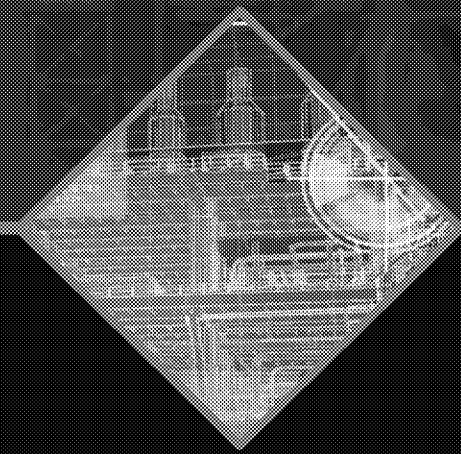
## Release Scenario

- Key parameters
  - Rate of release
  - Locations
  - Unit parameters



## Standard

- Performance standard that must be met if MHF is released



## Demonstration

- Demonstrate standard is met through
  - Modeling
  - Testing

# Staff is Seeking Direction

- Continue with approach based on direction from Refinery Committee
  - Develop rule or MOU that requires refineries to:
    - Phase-out MHF within 5 to 7 years; or
    - Demonstrate, based on enhanced mitigation measures, that they meet a performance standard (to be developed) that ensures a consequential release will not impact the community